pH Responsive Microcapsules for Corrosion Control

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Abstract

The best coatings for corrosion protection provide not only barriers to the environment, but also a controlled release of a corrosion inhibitor, as demanded by the presence of corrosion or mechanical damage. NASA has developed pH sensitive microcapsules (patent pending) that can release their core contents when corrosion starts. The objectives of the research presented here were to encapsulate non-toxic corrosion inhibitors, to incorporate the encapsulated inhibitors into paint formulations, and to test the ability of the paints to control corrosion. Results showed that the encapsulated corrosion inhibitors, specifically $Ce(NO_3)_3$, are effective to control corrosion over long periods of time when incorporated at relatively high pigment volume concentrations into a paint formulation.

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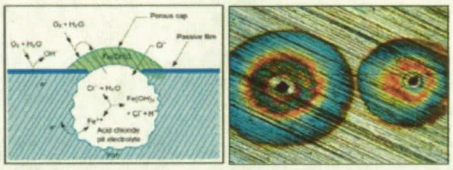
Electrochemical Nature of Corrosion

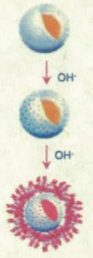
Corrosion is largely an electrochemical phenomenon because, in most cases, it involves the transfer of electrons between a metal surface and an aqueous electrolyte solution. For instance, when iron corrodes in near neutral environments, the typical electrochemical reactions are:

- Overall Reaction
  $$2H_2O + O_2 + 2Fe \rightarrow 2Fe^{2+} + 4OH^-$$
- Anodic Reaction
  $$Fe \rightarrow Fe^{2+} + 2e^-$$
- Cathodic Reaction
  $$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$



basic pH conditions at localized corrosion cathodic sites

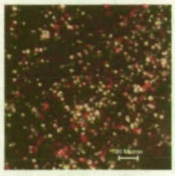
pH Sensitive Microcapsules



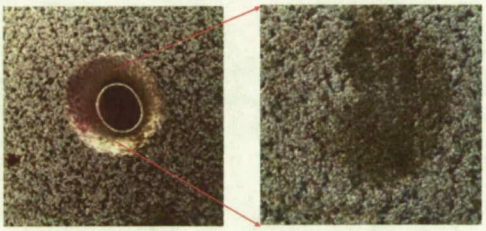
Microcapsule containing pH indicator (inhibitor, self healing agents)

The shell of the microcapsule breaks down under basic pH conditions

pH indicator changes color and is released from the microcapsule under basic conditions

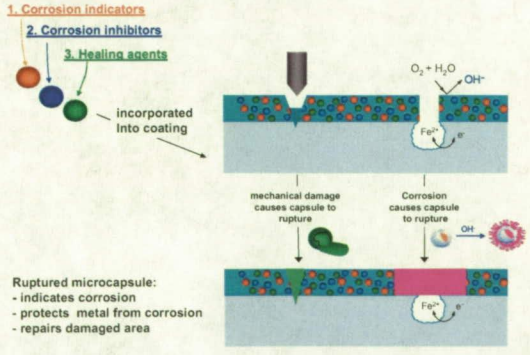


Color change observed when microcapsules in solution respond to basic pH conditions



Microcapsules in solution indicate the presence of localized corrosion on a carbon steel substrate

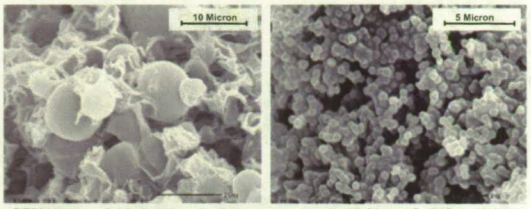
Smart Coating Concept



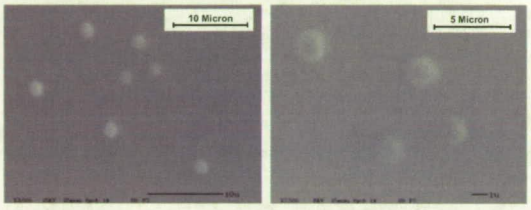
Ruptured microcapsule:
- indicates corrosion
- protects metal from corrosion
- repairs damaged area

Paint Formulation

Three microcapsule samples with different core contents were used for paint formulation. The control sample contained only inert solvent and the other two contained corrosion inhibitors: $Ce(NO_3)_3$ and Na_2MoO_4. Epon 828 was added into a dispersion of microcapsules in a solvent mixture followed by the addition of the amine curing agent, PACM. The amine was applied onto AA2024-T3 panels that were sandblasted and degreased before coating application. The coatings were allowed to cure under ambient conditions for 48 hours before any testing.



SEM images of dried microcapsules: empty capsules (left) and $Ce(NO_3)_3$ (right)

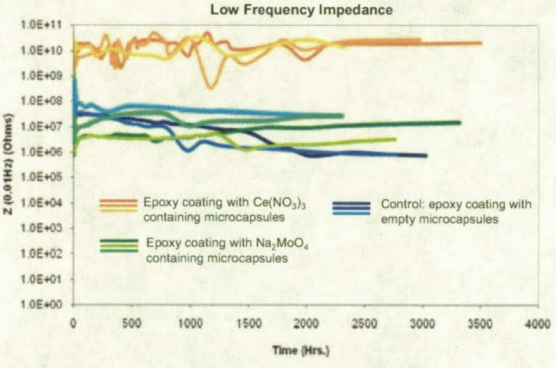


Microcapsules appear dispersed and stable inside an epoxy amine coating

Electrochemical Measurements

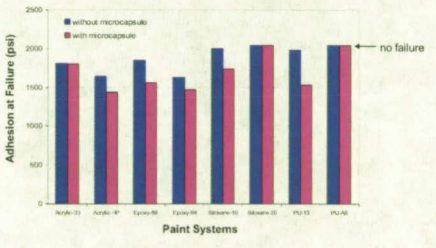
Detailed information regarding the condition of the coating was obtained using electrochemical impedance spectroscopy (EIS). The variation of the low frequency impedance data with time is shown below.

- Instrument: Gamry® PC-4 or FAS1
- Initial AC perturbation -10 mV rms; frequency range: 100,000 Hz to 0.01 Hz
- Electrolyte: dilute Harrison's solution (0.35% $(NH_4)_2SO_4$ and 0.05% NaCl)



Compatibility with paint systems

One concern regarding the inclusion of microcapsules into a paint system is their interaction with paint constituents which could result in lower adhesion. Test panels were prepared for 8 paints representing 4 paint systems: acrylic, epoxy, polyurethane, and siloxane. Adhesion tests (ASTM D4541-85(89) on these panels were performed using a pneumatic adhesion tensile testing instrument (PATTI) to measure pull-off strength.



Summary

- A smart coating system based on the electrochemical nature of corrosion has been developed using pH sensitive microcapsules.
- The pH sensitivity as well as the ability of the microcapsules to indicate localized corrosion at an early stage has been investigated.
- Beneficial corrosion protection has been provided by encapsulated corrosion inhibitors, specifically the $Ce(NO_3)_3$, over long immersions times.
- Results from adhesion tests indicated that, in most cases, the microcapsules had no significant effect (more than 15%) on paint adhesion properties when added to commercially available paints.